

**EXAMINATION OF CHANGES IN HYGROSCOPICITY AND CCN  
ACTIVATION EFFICIENCY DURING PARTICLE GROWTH  
EVENTS**

A Senior Scholars Thesis

by

CRYSTAL DEANN MCCLURE

Submitted to the Office of Undergraduate Research  
Texas A&M University  
in partial fulfillment of the requirements for the designation as

UNDERGRADUATE RESEARCH SCHOLAR

April 2010

Major: Meteorology

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Approved by:

Research Advisor:

Associate Dean for Undergraduate Research:

Don Collins

Robert C. Webb

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## ABSTRACT

Examination of Changes in Hygroscopicity and CCN Activation Efficiency During Particle Growth Events. (April 2010)

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The growth and evolution of newly formed atmospheric particles were examined using an array of instruments located at a rural site northwest of Houston, TX. The focused study described here was designed to evaluate the influence of nucleated particles on same day and next day CCN concentrations. An integrated differential mobility analyzer / tandem differential mobility analyzer / CCN counter was used to track the size, hygroscopicity, and cloud nucleating efficiency of the population of particles that formed during the morning and grew throughout day and into the night. As has been observed using similar instrumentation at other locations, the hygroscopicity of the recently formed particles exhibited a diel pattern having a maximum in the early afternoon and a minimum before sunrise. To attribute the growth and evolving properties of these particles to the responsible mechanisms, complementary measurements of gas phase precursors and oxidants, which were made concurrently to particle measurements, will be compared in a future project. Of particular interest would be the link between nighttime nitrate radical concentration and the rates at which the diameter of the particles

increased and at which their critical supersaturation decreased. Ultimately, these data can help constrain the relative importance of organic and inorganic precursors and of differing oxidants to the production of CCN in regions for which both anthropogenic and biogenic emissions sources are significant.

## **DEDICATION**

I would like to dedicate this paper and the research completed to my parents who have always pushed me to work harder and never leave anything unfinished.

## ACKNOWLEDGMENTS

First of all, I would like to extend tremendous gratitude to my advisor, Dr. Don Collins, for giving me the opportunity to work on this project along with all of the guidance and support that he has given throughout the project. This project would certainly not have been possible, let alone gone as smoothly as it did without your help.

I would also like to say thank you to my colleague and friend, Katelyn Johnson, for helping me with fieldwork, analyzing data and for all the times you helped me through the little fumbles in this project.

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Thank you Dr. Runjun Li for your help with programming the computers, I greatly appreciate everything you did.

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Finally, I would like to thank my parents, Nancy and Ed McClure, along with Devin

Light for their understanding when I was working on this project and could not be there with them.

## NOMENCLATURE

APS	Aerodynamic Particle Sizer
cc/min	Cubic Centimeters per Minute
CCN	Cloud Condensation Nuclei
CCNc	Cloud Condensation Nuclei Counter
CPC	Condensation Particle Counter
DMA	Differential Mobility Analyzer
$(Dp)_{peak}$	Peak Diameter
GF	Growth Factor
GHG	Greenhouse Gases
$\kappa$	Hygroscopicity Parameter (Kappa)
$\kappa_{CCN}$	Kappa Calculated by CCNc
$\kappa_{TDMA}$	Kappa Calculated by TDMA
$NO_3\bullet$	Nitrate Radical
$O_3$	Ozone
OPC	Optical Particle Counter
P	Pressure
$Q_{max}$	Maximum Flow Rate
$Q_{min}$	Minimum Flow Rate
R	Universal Gas Constant
S	Saturation Ratio



Sc	Critical Supersaturation
SFCA	Scanning Flow CCN Analysis
SOA	Secondary Organic Aerosols
SS	Supersaturation
$\Delta T$	Change in Temperature
$t_{\text{base}}$	Time at $Q_{\text{min}}$
$t_{\text{down}}$	Time between $Q_{\text{max}}$ and $Q_{\text{min}}$
$t_{\text{peak}}$	Time at $Q_{\text{max}}$
$t_{\text{up}}$	Time between $Q_{\text{min}}$ and $Q_{\text{max}}$
TDMA	Tandem Differential Mobility Analyzer
VOC	Volatile Organic Compounds

## TABLE OF CONTENTS

	Page
ABSTRACT .....	iii
DEDICATION.....	v
ACKNOWLEDGMENTS.....	vi
NOMENCLATURE .....	viii
TABLE OF CONTENTS .....	x
LIST OF FIGURES .....	xi
 CHAPTER	
I     INTRODUCTION .....	1
II    METHODS.....	5
Instrumentation .....	5
Programs .....	7
Data analysis .....	9
III   RESULTS .....	13
IV   CONCLUSIONS .....	16
REFERENCES .....	18
APPENDIX .....	20
CONTACT INFORMATION .....	27

LIST OF FIGURES

FIGURE	Page
1 Nucleation.....	20
2 Location of Lick Creek Park.....	21
3 Instrumentation Schematic .....	22
4 Kappa Illustration.....	23
5 Results .....	24
6 Graph (f) Back Trajectory .....	26

## CHAPTER I

### INTRODUCTION

Atmospheric aerosols are produced through direct emissions from biogenic and anthropogenic sources and through nucleation of new particles from precursor gases. These particles grow over time through condensation and coagulation, but most are removed from the atmosphere by either wet or dry deposition. They can also grow through aqueous phase production of sulfate, which is most often the dominant mechanism for sulfate production. Aerosols can, however, become cloud condensation nuclei (CCN) whose role is the largest uncertainty in future climate simulations. The effects of aerosols are largely dependent upon their size and composition which motivates work, like in this study and other recent studies, to understand what affects their growth and chemical evolution. Organic aerosols and especially secondary organic aerosols (SOA) have been shown to significantly increase the number of CCN in the atmosphere [VanReken *et al.*, 2005]. However, what we currently know is limited with respect to how these organic aerosols actually affect CCN concentration and their ability to act as CCN [VanReken *et al.*, 2005]. The influence of changing aerosol concentrations on cloud albedo and lifetime, however, is known to be dependent upon those particles that have grown enough to act as CCN and form cloud droplets. In many areas, growth rates have been observed to be linked strongly to condensation of SOA produced by reactions

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This thesis follows the style of *Journal of Geophysical Research - Atmospheres*.

involving biogenic and anthropogenic emissions and oxidants such as ozone,  $O_3$  and nitrate radical,  $NO_3\bullet$  [Russell and Allen, 2005; Fry *et al.*, 2009].

These processes in which aerosols affect the climate are mainly through their indirect effects as CCN. The indirect effect of aerosols on climate is very different from the warming caused by greenhouse gases because the magnitude (or radiative forcing) of the former is unlikely to change much in the next century, while that of the latter will increase significantly. Thus, it is tempting to focus just on greenhouse gases (GHG) if the aerosol influence is expected to be relatively stable. However, projections of the recent temperature record into the future require an understanding of the link between greenhouse gas and aerosol radiative forcing along with temperature. When aerosol particles grow large enough to become activated in the presence of a specific supersaturation of water vapor for their composition and size, they can become fog or cloud droplets which are known as CCN [Seinfeld and Pandis, 1998]. With more aerosols that can act as CCN there are, in turn, a higher number of cloud droplets in the cloud. Therefore, with more cloud droplets, the cloud albedo of solar radiation is higher which, overall, cools the climate. This would mean in an area with high concentrations of aerosols that have the potential to become CCN we get a higher cloud albedo. This indirect effect is complicated to identify because only a small fraction of the aerosol population in a given area will actually activate to become CCN and therefore affect cloud albedo. Changes in the number concentration of aerosols are observed to cause changes in the size and population of cloud droplets and consequently cloud albedo

[Seinfeld and Pandis, 1998]. If the current indirect effects of aerosols on climate could be quantified with certainty compared to that for GHG, the uncertainties in future climate changes would be drastically reduced and it would be possible to link future emissions scenarios with climate change consequences. The primary reason the impact of aerosols is still inadequately understood is that, unlike GHG that are uniformly distributed, aerosols are temporally and spatially heterogeneous and the handful of surface measurements currently made are insufficient to be directly used in radiative transfer models. The implications of this project and future projects in learning how nucleated particles behave and how the effects of precursor gases affect these particles is important for learning how they evolve, affect CCN concentrations and as a result cloud albedo and climate.

A similar project to this one conducted in the boreal forests of Finland demonstrated that there was a clear diel cycle of hygroscopicity with the growth factors being higher during the day than night and that this affected smaller particles more than larger ones. The researchers concluded based on the study that the gas phase precursors responsible for the growth of these particles changed from day to night [Ehn *et al.*, 2007]. Another study in a rural area of Virginia came to the same conclusions while tracking nucleation and following the hygroscopicity and growth of the nucleated particles [O'Halloran *et al.*, 2009]. Figure 1 shows a case of daily nucleation that happened over three days in Virginia. The change in hygroscopicity (or growth factor (GF)) and the soluble fraction of the particles from day to night could be explained by a change in precursor gases

affecting the nucleation mode particles.

This project has afforded an opportunity to use what we and others in previous case studies have learned about the growth and hygroscopicity of nucleated particles. In addition, a future project the relationship of growing particles with concurrent gas phase measurements of an important daytime and potential nighttime precursor gas, i.e.  $O_3$  and  $NO_3\bullet$ , respectively, will be made. The complimentary measurements of gas phase precursors and oxidants can help to identify which precursor gas and oxidant is affecting the size and hygroscopicity of nucleation mode particles. Of particular interest in this future project is the link between nighttime nitrate radical concentration and the rates at which the diameter of the particles increased and their critical supersaturation decreased. Ultimately, these data sets can help constrain the relative importance of organic and inorganic precursors and of differing oxidants to the production of CCN in regions for which both anthropogenic and biogenic emissions sources are significant.

## **CHAPTER II**

### **METHODS**

The measurements for this project were collected at Lick Creek Park in College Station, Texas beginning on September 23, 2009 and are ongoing. The instruments are housed in an air conditioned trailer near the equestrian entrance of the park. The area mainly consists of oak trees with light automobile traffic about ten meters away from the trailer and a large highway around three kilometers away to the southwest. The closest coal fired power plant is around 15 kilometers northeast of the park. Houston, which is also a major source of pollution, is approximately 121 kilometers to the southeast. Figure 2 shows a map of where the area of the experiment took place and in which direction the areas close by that could contribute to pollution seen at the site.

#### **Instrumentation**

A schematic of the instrumentation setup during this project is given in Figure 3. A Differential Mobility Analyzer (DMA) is used to separate out a specific size of particles. Two DMAs are housed inside the trailer located at Lick Creek Park. Two modes of operation using the aforementioned instrument are employed to characterize the continuously sampled aerosol. One of the modes is referred to as a DMA mode where only one DMA is used and the other mode is referred to as a Tandem Differential Mobility Analyzer (TDMA) mode where both DMAs are used. During the DMA mode, only the first DMA pulls sample flow from outside. Prior to entering the DMA, the



sample aerosol is dried in the dehumidifier and then goes through a charger that bring all of the particles to a uniform charge distribution. When the aerosol particles enter the first DMA they are separated out by size due to the ramping voltage inside the DMA that classifies certain particle sizes at specific voltages. After this, the sample flow is sent to the Condensation Particle Counter (CPC) where the particles separated out by the DMA are counted. During the DMA mode, the Cloud Condensation Nuclei Counter (CCNc) pulls in ambient air from outside. This mode is executed first because the peak of the distribution must be found in order to establish values for the TDMA mode. The program used to find the peak of the distribution is called a “peak-finder”. From the size that it determined as the peak, the TDMA separates out only that particular size of particle. During the TDMA scan, the sample flow is pulled in, dried and charged as before, but now the DMA only separates out the particle size corresponding to the peak in the just-measured size distribution. These particles in the sample flow are then sent to the second DMA, then to the CPC and CCNc. The path to the second DMA first passes through a humidifier that is enhanced by a Relative Humidity (RH) bottle. This bottle is filled almost full with distilled water and the water inside is heated so that the air being taken into the instrument from the bottle has a high RH. The RH probes that are located before the humidifier, and before and after the second DMA, are used to monitor the RH of the sample flow. Particle hygroscopicity is then measured as the second DMA measures the new size distribution of the particles and thus reveals how the aerosol particles have grown after humidification. This sample flow is then split between the CPC, where the concentration of particles is again measured, and the CCNc. The flow to

the CCNc changes over time due to specifications by the SFCA approach (detailed explanation provided in the Programs section of Chapter II) for scanning the CCN spectra. The sheath flow in the CCNc ranges from a  $Q_{\min}$  of 200 cubic centimeters per minute (cc/min) on average to a  $Q_{\max}$  of 1000 cc/min on average while the sample flow is 10% of the maximum and minimum sheath flow, respectively. The times used for flow scanning are calculated based on how long the TDMA scan will last. The Aerodynamic Particle Sizer (APS) compliments the DMA data because the size range for particles measured by the DMA is constrained between 0.01 and 0.75 microns. The APS can measure particles from 0.5 to 10 microns, which extends the measured total size distributions from just the nucleation and aiten modes measured by the DMA/TDMA to the full spectrum with the coarse mode included. The setup for the APS is detailed in Figure 3.

## **Programs**

The main differences between this project and others like it are the adjustments in the way we study the changes in size and properties of recently formed particles. In order to track these changes, we changed the way the CCNc measures CCN. This required changing the time resolution of the CCNc to be comparable with that of the changing particles and having the ability to track a mode of particles rather than simply making measurements of many different fixed sizes. Typically, a CCNc, as described in *Roberts and Nenes* [2005], would be operated with constant sample and sheath flows through a chamber where the temperature inside would rise by a prescribed amount ( $\Delta T$ ) from top

to bottom; those particles that activate during descent through the chamber are measured by the Optical Particle Counter (OPC) at the very bottom of the chamber. The  $\Delta T$  corresponds to a certain supersaturation (SS) at the fixed flow rates and during a scan of a set of different SS the  $\Delta T$  goes through a stepping pattern to measure the concentration of CCN at each SS. The problem with this technique, as described in *Moore and Nenes* [2009], is that the temperature stabilization is slow and the data were collected during the stabilization period is normally of no use and thrown out. What is proposed in the *Moore and Nenes* [2009] paper is a faster method for scanning the CCN spectra through the method of “Scanning Flow CCN Analysis” or SFCA. This project utilized the idea of SFCA and incorporates it into the programs used to run the instruments. Using the principle behind SFCA in order to increase the SS while keeping  $\Delta T$  constant we increased the flow rate linearly between a minimum and maximum flow rate ( $Q_{\min}$  and  $Q_{\max}$ , respectively) over a ramp period ( $t_{\text{up}}$ ). The opposite is true when decreasing the SS going from  $Q_{\max}$  to  $Q_{\min}$  during the period  $t_{\text{down}}$ . The flow is kept constant at  $Q_{\min}$  and  $Q_{\max}$  for a period of time,  $t_{\text{base}}$  and  $t_{\text{peak}}$ , respectively. The cycle starts off at  $Q_{\min}$  then moves through the periods  $t_{\text{up}}$ ,  $t_{\text{peak}}$ ,  $t_{\text{down}}$  and then to  $t_{\text{base}}$  and repeats [*Moore and Nenes*, 2009]. These cycles are the scans produced by the SFCA method. This process is completed in order to scan over multiple SS during a short period of time. From this idea of SFCA we built a program that would control the CCNc flow rate over the time intervals that are described above. The values chosen for this project were closely modeled after the values given in the aforementioned paper in order to be able to calibrate and compare our data to those observed by *Moore and Nenes* [2009]. The

program we created was then integrated with the TDMA program so that it would be able to control the CCNc flow rates based on the SFCA method. A program was also built that would calculate the correct  $\Delta T$ , minimum SS and maximum SS for certain  $Q_{\max}$ ,  $Q_{\min}$ , constant pressure (P) and a specified SS for a particular type of aerosol. This program was also incorporated into the ground TDMA program and controls the  $\Delta T$  automatically in the CCNc. The basis of the program was given in *Robert and Nenes* [2005] and *Lance et al.* [2006] as a way of approximating the dependence of supersaturation on the instrument's operating conditions. The equation that explained this dependence (equation 16 in *Lance et al.* [2006]) was reversed and introduced into a while loop to recursively give the  $\Delta T$  for a given SS specific to a certain type of aerosol. The link between this calculation for the CCNc and what is measured by the DMA and TDMA lies in the fact that we assume that the aerosols we are measuring are much like ammonium sulfate in their composition. If we know the diameter of the particle we are looking at and the assumption stated previously we can calculate the specified SS for the sample aerosol we are analyzing.

## **Data analysis**

### *Hygroscopicity parameter, $\kappa$*

In order to confirm our results, we used two different methods to measure hygroscopicity. The parameter  $\kappa$  was used to represent the hygroscopicity of the particles in each method. Figure 4 illustrates how each  $\kappa$  was determined. As detailed in *Petters and Kreidenweis* [2007], the hygroscopicity parameter,  $\kappa$ , represents a quantitative

measure of aerosol water uptake characteristics and CCN activity for aerosols. This is used to determine if an aerosol particle will grow and/or activate as a CCN particle by whether the particle contains hydrophobic or hydrophilic properties. Even though most aerosols are made up of a mixture of inorganic and organic constituents which can be hydrophobic or hydrophilic; values of  $\kappa$  can still be determined experimentally for these heterogeneous particles by fitting CCN activity or hygroscopicity growth factor data [Petters and Kreidenweis, 2007]. The usual range of  $\kappa$  for atmospheric particulate matter is between 0.1 and 0.9 with a higher number indicating a greater affinity for growth and/or water uptake (hygroscopic) and a lower number indicating a lesser affinity for the same (less/non-hygroscopic).

#### *TDMA based $\kappa$*

As explained above,  $\kappa$  can be determined experimentally by interpreting the hygroscopic growth factor data. These measurements can be taken during TDMA scans as described in Chapter II. This collected data can then be used through Köhler theory, as described in Petters and Kreidenweis [2007], to determine a single hygroscopic parameter,  $\kappa$ , during the stage at which the TDMA system is scanning the particles. During the analysis portion of this project, we built a program that would determine  $\kappa$  from the TDMA's hygroscopic growth factor measurements collected based on equations 1 through 6 in Petters and Kreidenweis [2007]. This was executed by first finding the peak diameter for the size distribution which was done by the "peak finder" program detailed in Chapter II (in the section entitled Instrumentation). Then the TDMA program

collected the peak growth factor for the diameter separated out by the first DMA and the “peak finder”. These sets of data were then combined by reversing equation 6, which uses dry and wet diameters for the particle to find the  $\kappa$  value, from *Petters and Kreidenweis* [2007] to solve for  $\kappa$  instead. Plugging in the peak diameter for  $D_d$  (dry diameter) and how large the particles had grown in relation to the growth factor in for  $D$  (wet diameter) we were able to solve for  $\kappa$ . The other values used in this equation were either given in the text, such as  $\sigma_{s/a}$  and  $T$ , or were constants ( $R$ ,  $M_w$  and  $\rho_w$ ). However, the saturation ratio ( $S$ ) was provided from the set value for the TDMA which was around 0.9. This calculation gave us the hygroscopicity parameter specific to the TDMA measurements,  $\kappa_{TDMA}$ , which are shown in Figure 5, in conjunction with the  $\kappa$  measurements made by the CCNc and the peak diameter as given from the “peak finder” program.

#### *CCNc based $\kappa$*

The principle for determining the hygroscopicity parameter based on the measurements taken by the CCNc was made by fitting the CCN activity data as described previously. This data was only available for the size selected particles during the TDMA scans described in Chapter II. The equations we used to find  $\kappa_{CCN}$  were given in *Petters and Kreidenweis* [2007] labeled as equation 10. Before we could calculate  $\kappa_{CCN}$  itself, we had to build a program that could take in the measurements of CCN activity that were made during the up and down scans of the SFCA program. The program designed discarded the CCN measurements during the DMA scan in view of the fact that they

were not made from the size selected by the “peak finder” program but were of ambient aerosol. This program, hence forth referred to as CCN analysis, also took the measurements from the TDMA scan, separated the up and the down scan data, fitted the data to a curve as a function of supersaturation versus concentration and finally found the 50% mark of the supersaturation,  $S_c$ . Critical supersaturation,  $S_c$ , is the saturation at which a particle transitions from an equilibrium state with its environment to an activated state [Seinfeld and Pandis, 1998]. This suggests that once a particle crosses the  $S_c$  point it will continue to grow larger and larger until some other force acts upon it. This also means that once the particle transitions past the  $S_c$  point it is activated and can become a CCN. With this knowledge of the  $S_c$  for each scan of particles we can use equation 10 from Petter and Kreidenweis [2007] in conjunction with the peak diameter given by the “peak finder” program to determine  $\kappa_{CCN}$ . The same values for  $\sigma_{s/a}$  and  $T$  used in calculating  $\kappa_{CCN}$  were used in calculating  $\kappa_{TDMA}$ . Similarly, the constants,  $R$ ,  $M_w$  and  $\rho_w$ , did not change between the two calculations. Another program was built to take in the values determined by the CCN analysis program and the peak diameter from the peak finder and run through equation 10 for each usable TDMA scan. This data is also plotted along with  $\kappa_{TDMA}$  and the peak diameter  $(Dp)_{peak}$  as determined by the peak finder program in Figure 5.

## CHAPTER III

### RESULTS

The graphs (a)-(f) shown in Figure 5 are plotted as function of fractional days of the year during the months of November through December 2009. The left axis is on a logarithmic scale and a function of hygroscopicity parameter ( $\kappa$ ). The right axis is a function of peak diameter size,  $(Dp)_{\text{peak}}$ . The black triangles show values of  $(Dp)_{\text{peak}}$ , while the red and blue circles show values of  $\kappa_{\text{CCN}}$  and  $\kappa_{\text{TDMA}}$ , respectively. The graphs in Figure 5 also show the approximate separation of day and night by bands of white and grey, respectively. Typically the hygroscopicity of particles, as represented by the parameter  $\kappa$ , should peak in the early afternoon and be at a minimum right before sunrise. This expected trend is evident in all of the models (a-f) in Figure 5. The jumps in  $(Dp)_{\text{peak}}$  seen in Figure 5 are due to a change in peak diameter determined by the peak finder program. The reason for this could be either there were two modes that were present and comparable in concentration or a new mode became prominent and the program shifted to this new size. The former example can be seen in Figure 5 graph (c) during the nighttime measurements for day 362 and the latter in Figure 5 graph (a) during the daytime measurements at around 306.6. Graph (a) shown in Figure 5 is plotted through two complete days. It shows a good example of how  $\kappa$  or hygroscopicity decreases at night. What is interesting though is that the peak diameter of the mode being tracked is still growing even though the particles are becoming less hygroscopic. This would indicate that something less hygroscopic is condensing onto the particles



being measured and that is why the size is still increasing but the ability for the particles to take on water is decreasing. A closer look at this can be seen in graph (b) in Figure 5 where we are only looking over one day. An even more general look can be seen in graph (c) in Figure 5 where we are examining these parameters over three and a half days. The differences between  $\kappa_{CCN}$  and  $\kappa_{TDMA}$  seen in Figure 5 in graphs (a-f) could be from the way each instrument measures the respective  $\kappa$ . However, this difference seems to be small and the slope of each is generally similar. This would indicate the trend of hygroscopicity during the day and night, what we are most interested in, seems to be accurate when comparing the two different types of measurements of  $\kappa$  made by the CCNc and TDMA. From Figure 5, graphs (d) and (e) show the same growth during the night even though  $\kappa$  is decreasing as seen in the previously mentioned graphs. In each the particle is tracked for a full day and the trends mentioned previously can be seen clearly. Though in all the other graphs mentioned  $\kappa_{CCN}$  is higher than  $\kappa_{TDMA}$ , in graph (f) seen in Figure 5  $\kappa_{CCN}$  dips below  $\kappa_{TDMA}$ . This could have been caused by the meteorological conditions seen on that day. Figure 6 shows the back trajectory on December 31, 2009. This shows where the air came from as of 24 hours before the date mentioned in order to get to College Station, TX. What can be seen are strong winds out of the west that are taking air and particulates from the west. However, the east winds also get caught in this strong westerly wind as it moves in and get pushed back towards the east. This flow of air from both the east and the west could give two sources for particulates and/or a mixture by condensation on each other. With the winds coming in from the west being from an arid location and the winds from east Texas bringing in

volatile organic compounds (VOCs) from the forests this could account for shifting diameter sizes and anomaly readings by the CCNc and TDMA when determining  $\kappa$  values. We still see the expected decrease at night and increase during the day of hygroscopicity in graph (f) along with the steady increase of diameter during the night as well.

## CHAPTER IV

### CONCLUSIONS

An experiment, primarily using a DMA, TDMA and CCNc, was conducted in order to determine the size, hygroscopicity and cloud nucleating ability of aerosol particles as they grew during the day and into the night. The project took place at a rural location northwest of Houston starting on September 23, 2009 and is ongoing. This project looked specifically at whether particles grew at night and if they did whether their hygroscopicity (or  $\kappa$  value) was increasing or decreasing. This was done by looking at  $\kappa$  values determined by both the CCNc and TDMA. The reason for using both  $\kappa$  values which were measured differently by each instrument was in order to compare the trends and determine accuracy. Figures 5 and 6 show the results determined during the project. These results were, overall, consistent with what would be expected for the diel pattern of hygroscopicity. Namely, hygroscopicity, or as represented by  $\kappa$  in this project, should have a maximum during the early afternoon and have a minimum immediately before the sun rises. What was specifically examined in the study was the fact that we noticed even though the hygroscopicity of the particles decreased at night, the peak diameter of the particles was still increasing. This would suggest that something less hygroscopic, which would decrease the overall hygroscopicity of the particle, was condensing on the aerosol particles at night. What was suggested was that the precursor gas  $\text{NO}_3\cdot$  was reacting with something on the particle and then condensing onto these aerosol particles at night and decreasing their hygroscopicity. Normally, what would contribute to the

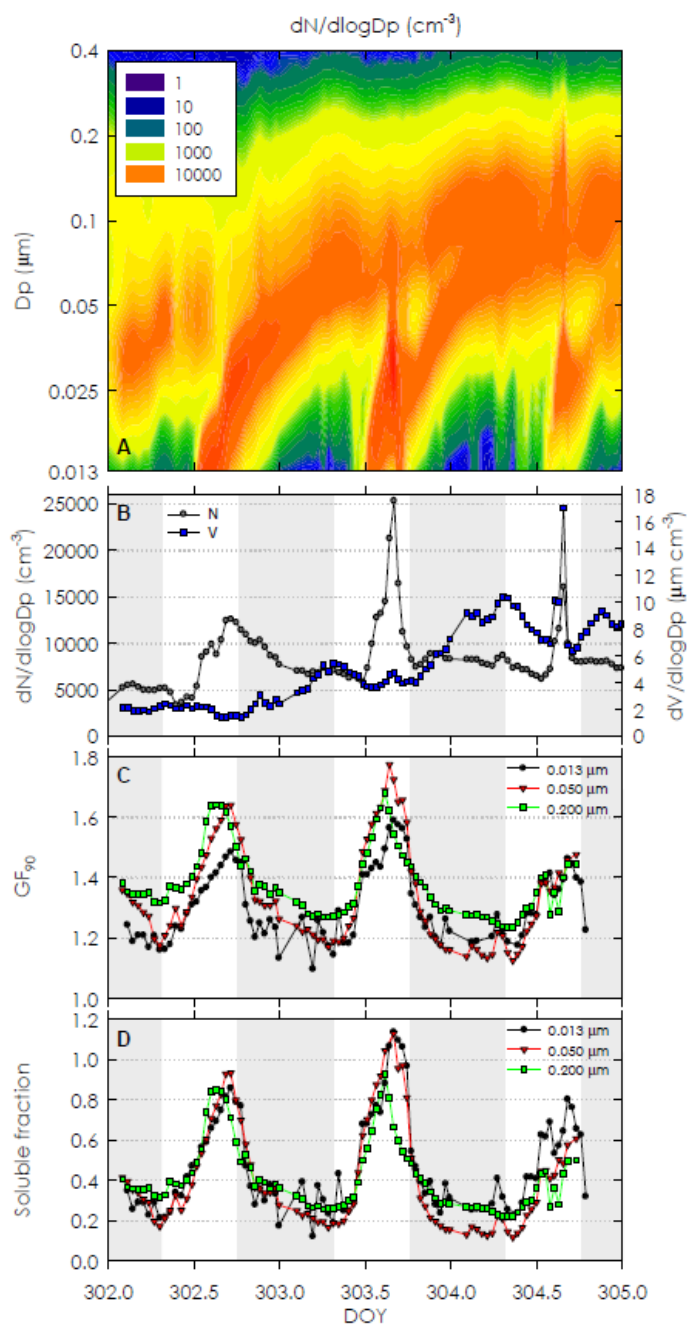
reduction the hygroscopicity would be organics and in particular biogenics. These results will be examined further in a future study by investigating gas phase measurements of precursor gases at night and during the day to determine which gases affect the hygroscopicity of the particles. With this study, which provide results of increasing particle diameter at night, and gas phase precursor measurements, the effects of the measured gases on aerosols can be experimentally explained and help to determine overall impacts on CCN concentrations.

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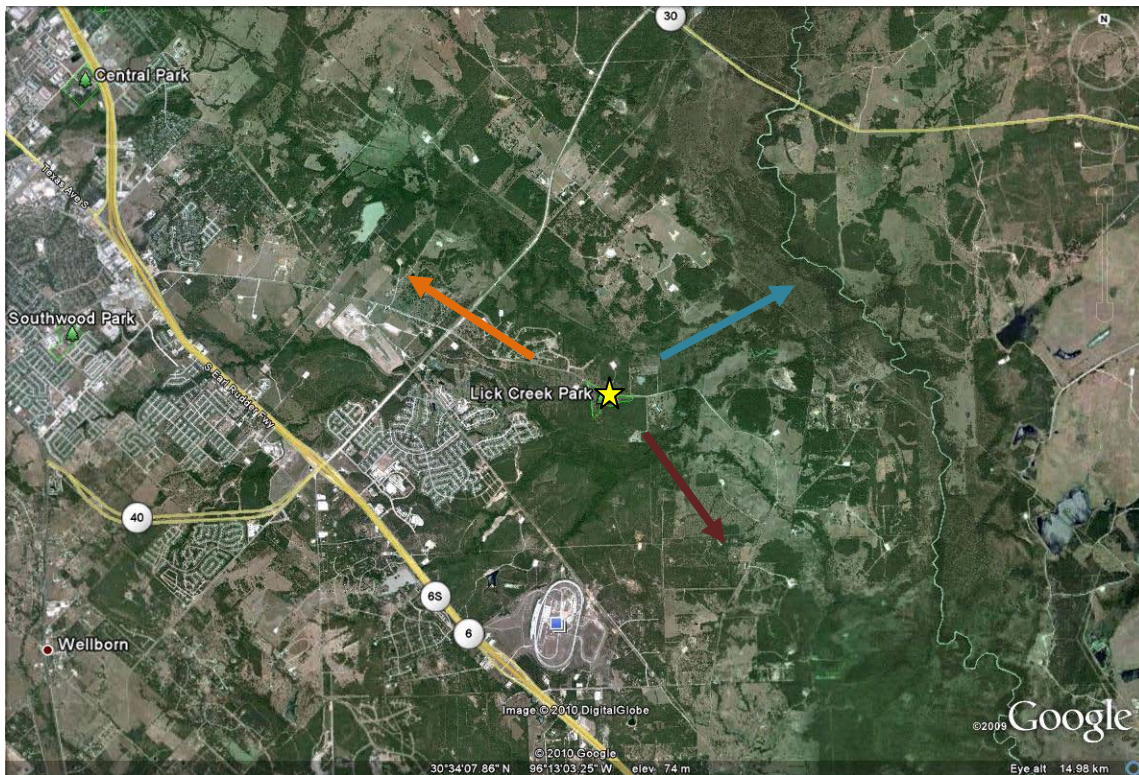
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## APPENDIX

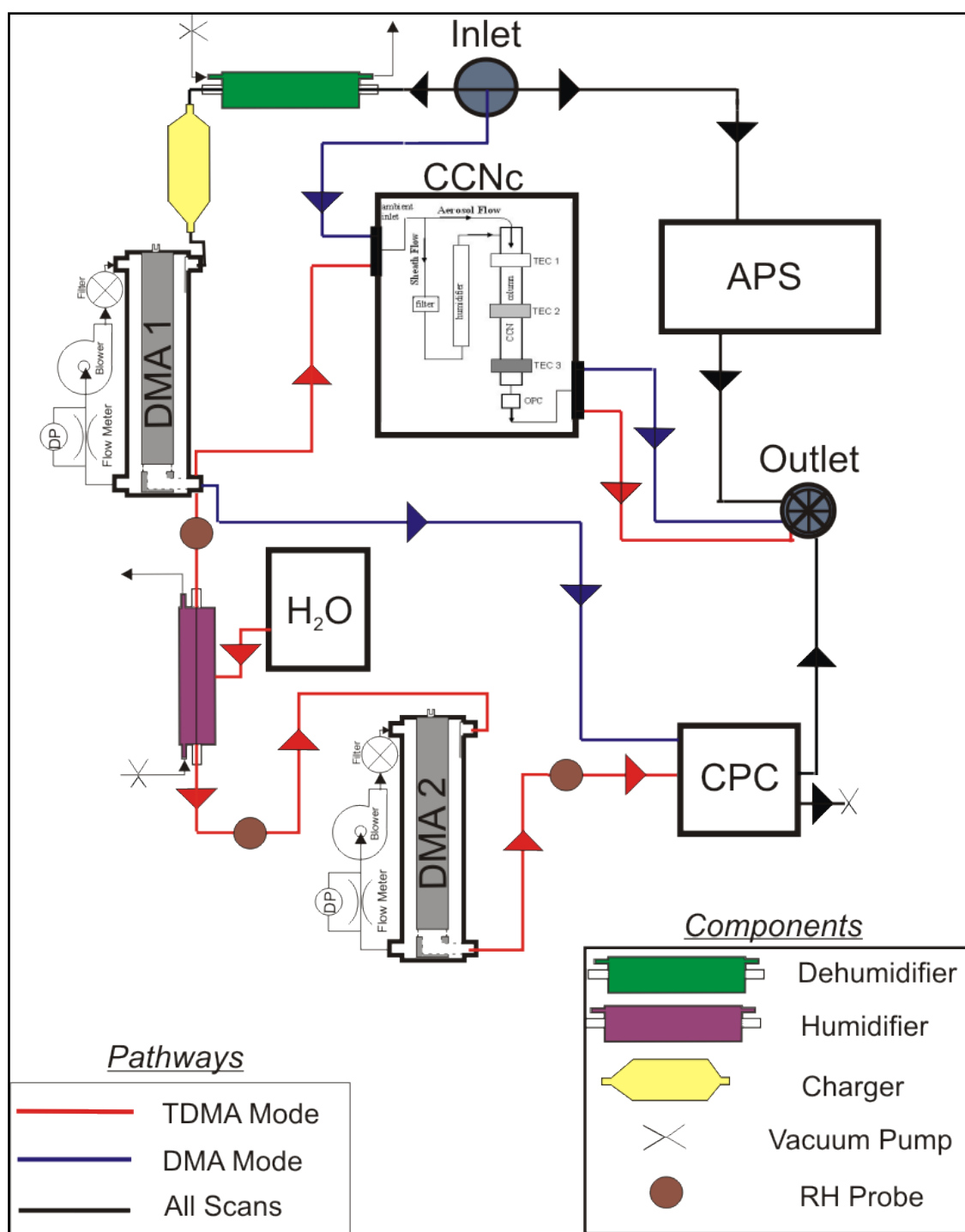


**Figure 1. – Nucleation** Three day case study showing nucleation events between October 29-31, 2006 in a rural area of Virginia. (A) Size-resolved number concentration, (B) total number concentration, (C) GF for three particle diameters (0.013, 0.05, and 0.200  $\mu\text{m}$ ), and (D) calculated soluble fraction. Nighttime is indicated by shading between sunrise and sunset [O'Halloran *et al.*, 2008].

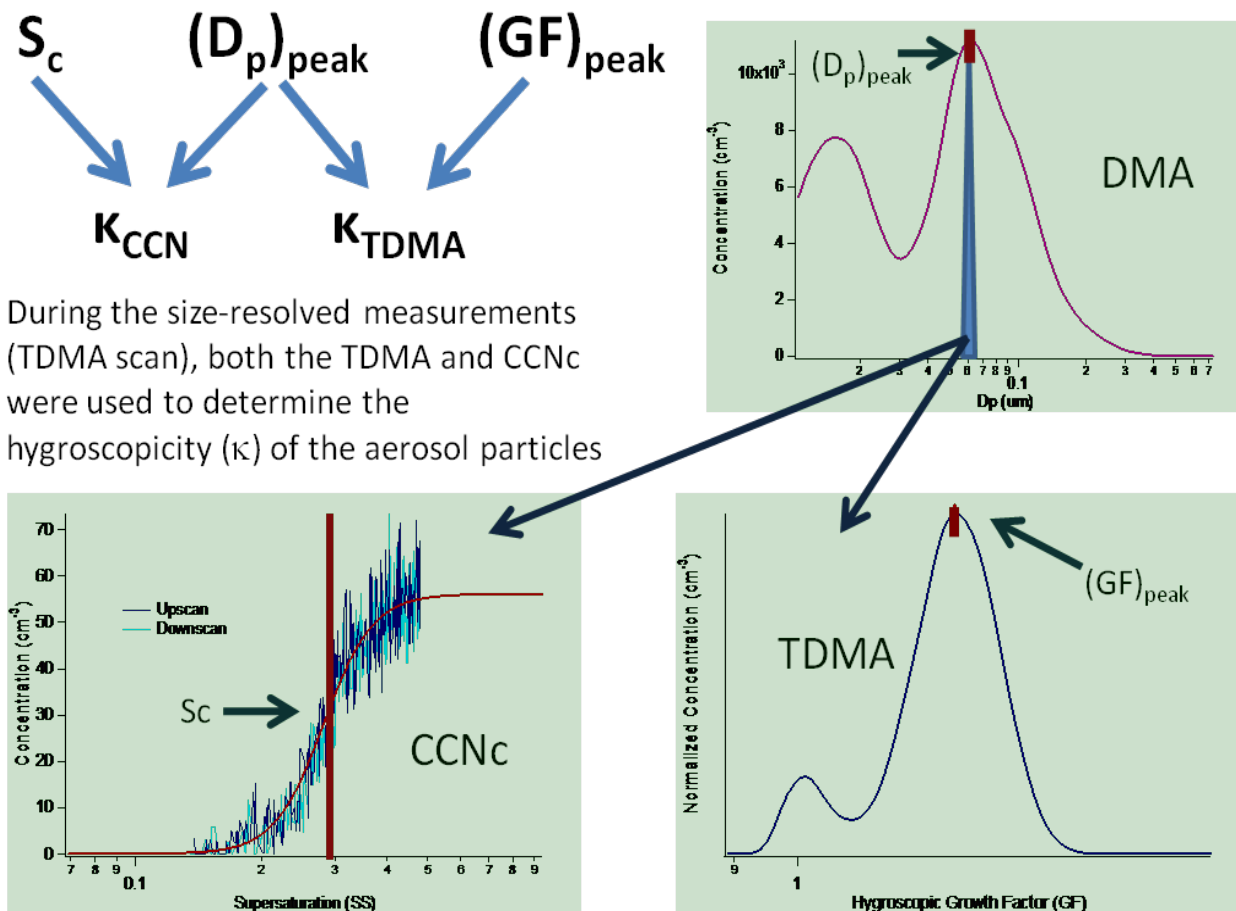


**Figure 2. Location of Lick Creek Park** The location of the park is indicated by the yellow star. The orange arrow points towards the Bryan/College Station area. The blue arrow points towards the Gibbons Creek power plant. Also, the red arrow points towards the Houston area.

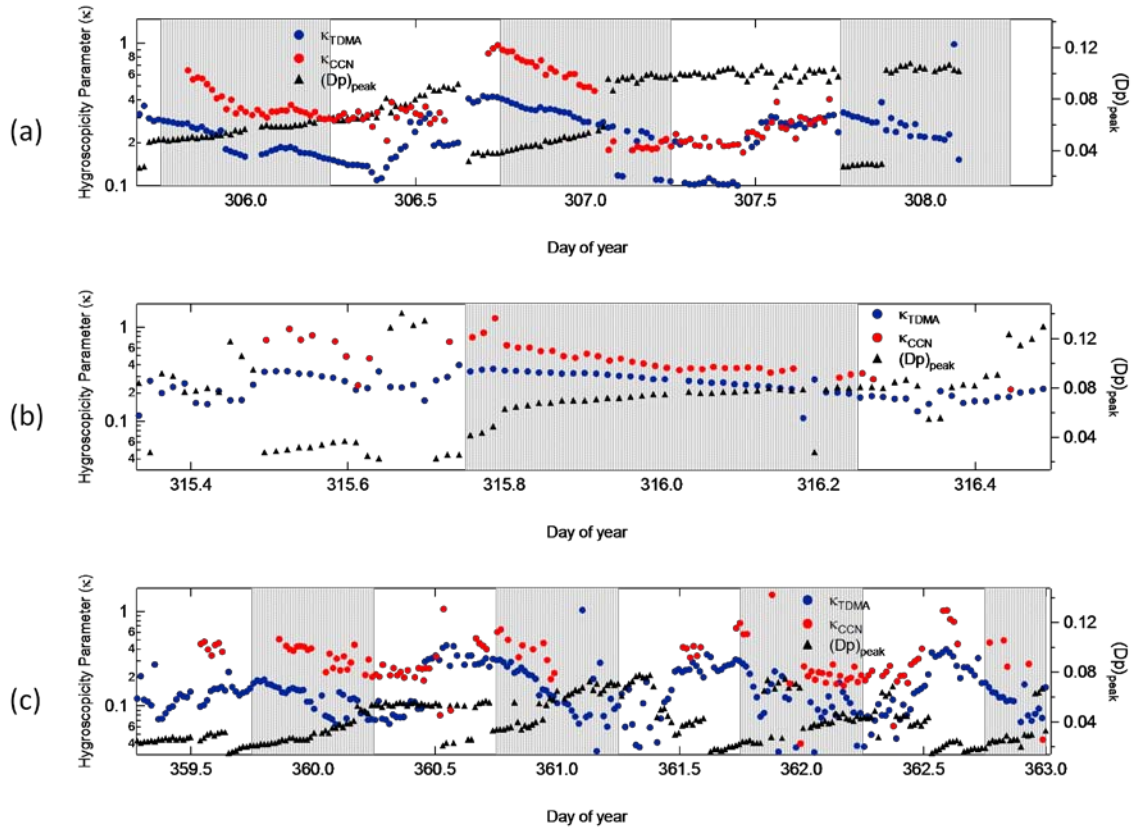




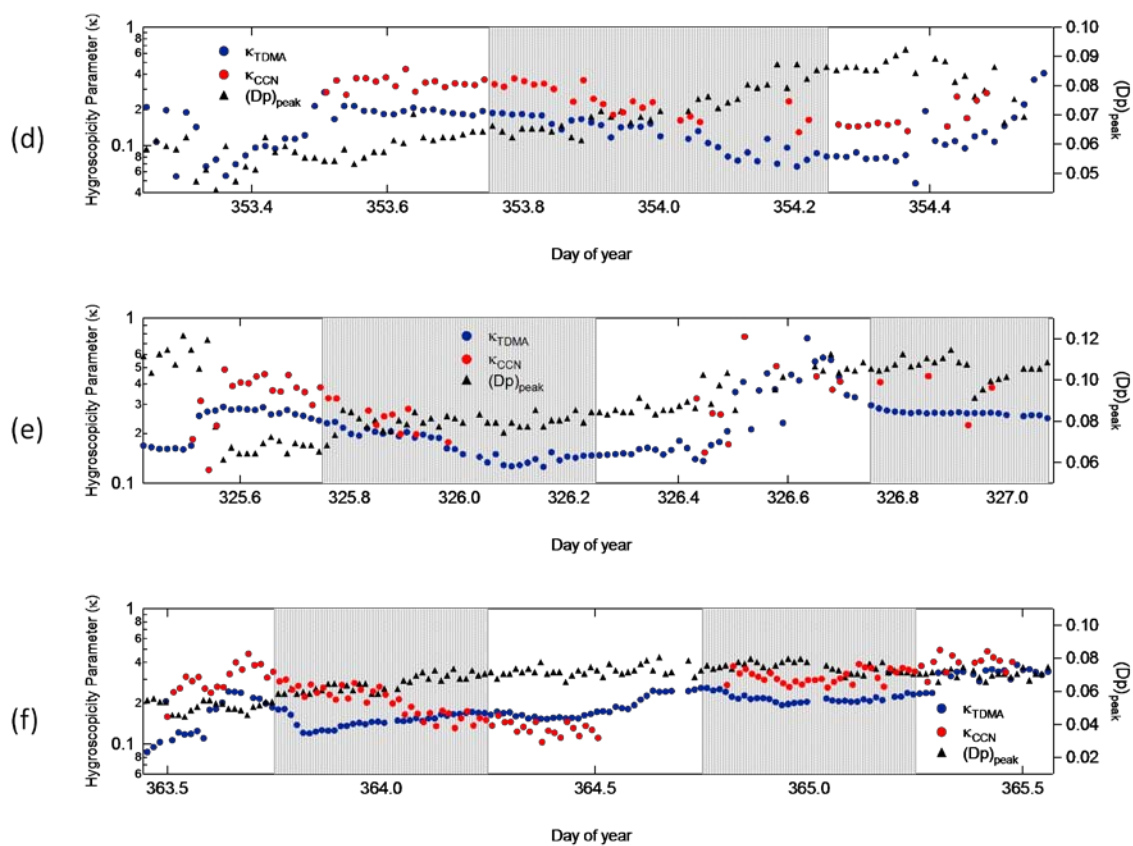
**Figure 3. – Instrumentation Schematic** An illustration of the Lick Creek Park setup. The red pathways only occur when the programs run a TDMA scan, the blue pathways occur only when the programs run a DMA scan and the black pathways are running continuously through all scans. CCNc schematic courtesy of Robert and Nenes [2005].



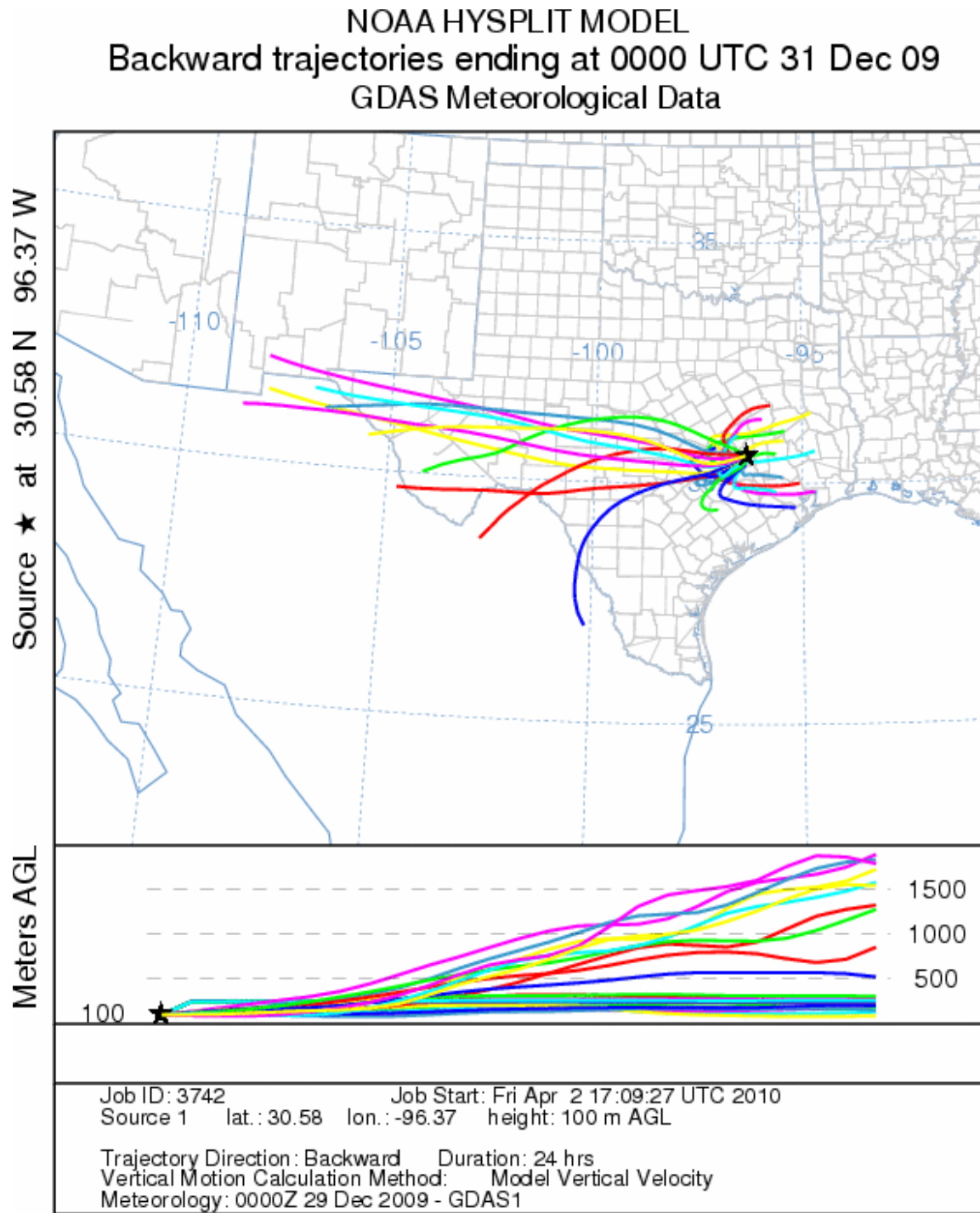
**Figure 4. Kappa Illustration** In the upper left corner, the graphic shows the parameters taken from the TDMA and CCNc data and how they combine to determine each  $\kappa$ . The upper right-hand corner provides a graph of a typical size distribution from a DMA scan where the peak diameter is found by the peak finder program and the blue band illustrates the sizes separated out during the DMA scan. The graphs on the bottom show how the size band separated out is used in the CCNc and TDMA to determine their parameters to calculate their respective  $\kappa$  parameters.



**Figure 5. Results** The graphs above show the results from this project graphed versus fraction day of year. The  $(Dp)_{peak}$  calculated by the peak finder program is graphed as black triangles. The  $\kappa_{TDMA}$  results are graphed as blue circles. Also, the  $\kappa_{CCN}$  results are graphed as red circles. The approximate distinction between day and night is indicated by white and grey bands, respectively.



**Figure 5. continued.**



**Figure 6. Graph (f) Back Trajectory** This graph shows where the air came from 24 hours out on December 31, 2009 in College Station, TX. The model is predicting these results using a ground level site of origin at 100 m. This graph was made using the NOAA Air Resources Laboratory's online model of Hysplit.

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